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Second Hyperpolarizability of Carbon Tetrachloride

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Background

Although present theories of nonlinear optics agree with observed behavior in simple atoms such as helium, more complex molecules containing many electrons, such as carbon tetrachloride (CCl_4), cannot consistently be described by theory. Through experimental analysis of nonlinear materials, a new, more sophisticated model for describing their properties could be realized. The purpose of our experiment was to measure the nonlinear behavior of the second harmonic signal generated from CCl_4 and to compare the results with the prediction by the CCSD(T) molecular model.

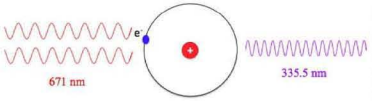

Figure 1: Second harmonic generation occurs when two fundamental frequency photons are incident upon and absorbed by a molecule with nonlinear properties. The resulting emitted photon has twice the frequency of the fundamentals.

Materials with nonlinear properties can convert light from one frequency to another, allowing for generation of many different frequencies from a single source. We measured second-harmonic generation, a nonlinear process in which two light waves of equal frequency are combined into a single light wave with double the frequency of either initial wave. The experiment utilized static electric field induced second-harmonic generation (ESHG) to produce a measureable second-harmonic signal from CCl_4. The signal was compared with the signal from nitrogen, a gas of known second hyperpolarizability γ, to determine the value of γ for CCl_4. Our γ_{CCl_4} value was compared to previously measured values at varying frequencies and with the prediction by the CCSD(T) mathematical model using the 31G(3d)+pd basis set, the highest approximation by reference 2.

The relevant equation for the second hyperpolarizabilty is given by the Taylor series expansion of the total electric dipole moment with respect to the local electric field E.

$$\mu_{total} = \mu + \alpha E + \beta E^2/2 + \gamma E^3/6 + \ldots$$

In the presence of a static electric field E_0 and an electric field E_w varying with frequency w, the γ term is given by:

$$\frac{\gamma E^3}{6} = \gamma[E_0 + E_w\cos(wt)]^3 = \gamma[E_0^3 + 3E_0^2E_w\cos(wt) + 3E_0E_w^2\cos^2(wt) + E_w^3\cos^3(wt)]$$

$3E_0E_w^2\cos^2(wt) = \frac{3E_0E_w^2}{2}[\cos(2w)+1]$ is responsible for the second harmonic signal generated in our experiment.

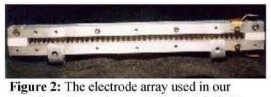

Figure 2: The electrode array used in our experiment to produce a static electric field.

Typically, the second-harmonic wave and the fundamental wave travel at different speeds through the nonlinear medium. As the length of the medium is increased, the second-harmonic waves generated at the beginning and the end of the sample get progressively farther out of phase, interfering perfectly destructively at the coherence length of the sample. ESHG allows for periodic phase matching in which the static field reverses in sign at length intervals equal to the coherence length of the sample, causing a phase shift of π radians in the generated second-harmonic wave, and therefore causing all second harmonic waves to be generated in phase with each other. The coherence length of the sample is adjusted to match the spacing of the electrodes by changing the density of the sample.

Apparatus

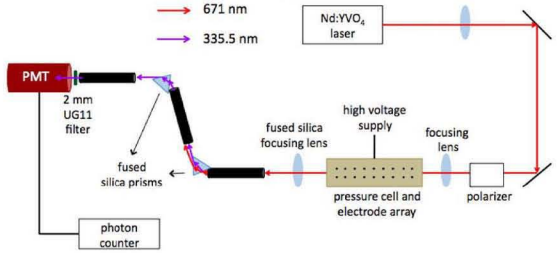

Figure 3: A schematic diagram of our experimental setup. Fused silica optics allow for transmission of UV light.

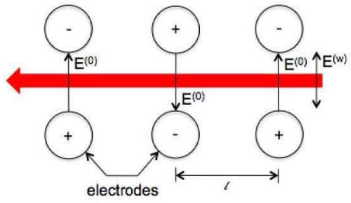

Figure 4: The static electric field generated by the electrode array is determined by the high voltage input. The periodic reversal of the sign of the field allows for optimal phase matching when the pressure is set to give a coherence length comparable to the length of the spacing between the electrodes. The enhanced amplitude of the signal due to phase matching varies by the square of the number of pairs of electrodes. The array used in our experiment contained 150 pairs of electrodes separated by 2.692 mm.

Data & Analysis

We performed our experiments by taking second-harmonic signal measurements for triplets of N_2 gas, a mixture of N_2 and CCl_4 gases, and N_2 gas. The decision to measure the N_2 signal before and after the CCl_4 signal allowed us to monitor the power fluctuations and possible mode changes of the laser. Since the second- harmonic signal varies with the square of the power, changes in the power output can significantly alter the signal. A change in mode affects the intensity profile of the beam, which also effects the second-harmonic signal. To reduce the error from changes in power and mode, triplets in which the peaks for N_2varied by amounts greater than counting statistics could account for, were discarded.

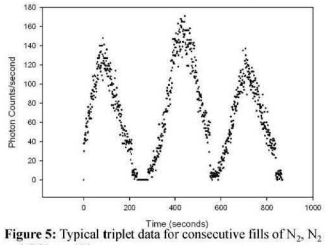

Figure 5: Typical triplet data for consecutive fills of N_2, N_2 and CCl_4 and N_2.

The peak signal value and pressure were approximated by a quadratic equation. Because each peak was not perfectly parabolic, a better approximation was obtained by only analyzing the top fifty percent of the data. This method also accounted for short power fluctuations of the laser by averaging over a range of pressures.

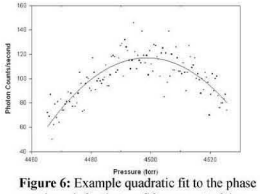

Figure 6: Example quadratic fit to the phase match peak for the top fifty percent of the second-harmonic signal from N_2.

Results

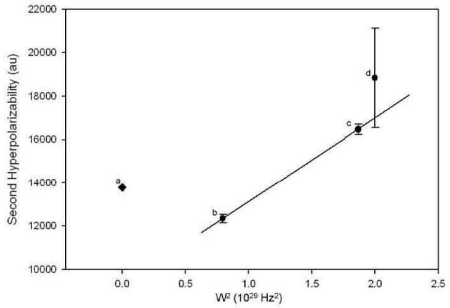

Figure 7: A linear relationship was observed between the second hyperpolarizability and the square of the frequency. The large error bar for our data d was caused primarily by fluctuations in laser beam propagation. Data point a was computed using the CCSD(T) model with basis set 31G(3d)+pd and was not included in the linear regression. [a]Reference 2. [b]Reference 3. [c]Reference 4. [d]This work.

A linear relationship is expected between the square of the frequency and the second hyperpolarizability. Therefore, a linear regression, weighted by the error bars, was obtained for all experimentally measured points. The static second hyperpolarizability determined by our fit was γ_s = 9268 375 au.

Assuming ideal gas behavior for both nitrogen and carbon tetrachloride, the ratio of phase match densities was calculated to be ρ_{N_2}/ρ_{CCl_4} =9.8375 0.1127. The observed phase match pressure for nitrogen was 4506 2 torr.

Conclusion

The value we obtained for γ_{CCl_4} agrees with previous experiments, which provides further evidence that these results are within their quoted margins of error.

The value of γ_s derived from the best fit line is not consistent with the value expected from the CCSD(T) method using a 31G(3d)+pd basis set. The two values of γ_s differ by 33%. The 4% error in our calculated value for γ_s does not account for this discrepancy, suggesting that current modeling techniques for nonlinear optics are unreliable.

To further the study of the nonlinear properties of CCl_4 and other molecules, one would like to eliminate error due to power and mode fluctuations by testing with a more stable laser. Also, performing the experiment at multiple fundamental frequencies will give a more accurate best fit line for w^2 versus γ_{CCl_4}. A more accurate γ_s value would provide a better foundation for refining current molecular models.

Acknowledgements

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